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## **THE EVOLUTION PROCESS OF NON-EQUILIBRIUM THERMODYNAMIC SYSTEMS**

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**Keywords:** non-equilibrium thermodynamics, hysteresis, processes far from equilibrium, entropy production, Earth evolution branches.

**Abstract.** The conditions that determine the evolution process in both isolated and open non-equilibrium thermodynamic systems are analyzed. Special attention is paid to open non-equilibrium systems that are far from equilibrium. It has been shown by experiments and calculations that non-equilibrium processes occurring in hydrodynamics, heat transfer, aerodynamics, magnetism, heterogeneous catalytic and homogeneous periodic chemical reactions, in biological systems (in the cell membrane, protein and algae cell) obey to the same general laws of state change of non-equilibrium thermodynamic systems in their evolution process. The basis of these laws is a general principle formulated in the form of an axiom about the processes perfection pursuit in nature. Schemes of evolutionary processes of non-equilibrium thermodynamic systems having both several non-overlapping and overlapping stationary states are presented. In conclusion, the obtained laws of the hysteretic process of non-equilibrium thermodynamic systems evolution are shown on the example of the Earth's atmosphere with all kinds of organisms living in it. Based on this, it is concluded that ice age and interglacial periods of the Earth's life are two branches of its evolution. On the lower branch of the hysteresis loop, with a lower entropy production, the evolution of the system proceeds according to the Clausius thermodynamic principle by the formation of increasingly complex structures with enlarging values of their entropy, which does not contradict Darwin's evolution theory.

## **ПРОЦЕСС ЭВОЛЮЦИИ НЕРАВНОВЕСНЫХ ТЕРМОДИНАМИЧЕСКИХ СИСТЕМ**

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**Ключевые слова:** неравновесная термодинамика, гистерезис, процессы далекие от равновесия, производство энтропии, ветви эволюции Земли.

**Аннотация.** Проанализированы условия, определяющие процесс эволюции как в изолированных, так и открытых неравновесных термодинамических системах. Особое внимание уделено открытым неравновесным системам, далеким от равновесия. Экспериментально-расчетным путем показано, что неравновесные процессы, протекающие в гидродинамике, теплообмене, аэродинамике, магнетизме, гетерогенных каталитических и гомогенных периодических химических реакциях, в биологических системах (в мембране клетки, белке и клетке водоросли), подчиняются одним и тем же общим закономерностям изменения состояний неравновесных термодинамических систем в процессе их эволюции. В основе этих закономерностей лежит общий принцип, сформулированный в виде аксиомы о стремлении к совершенству процессов в природе. Представлены схемы процессов эволюции неравновесных термодинамических систем, имеющих как несколько неперекрываемых, так и перекрываемых стационарных состояний. В заключении полученные закономерности гистерезисного процесса эволюции неравновесных термодинамических систем переносятся на атмосферу Земли с живущими в ней всевозможными организмами. На основании этого делается вывод, что ледниковый и межледниковый периоды жизни Земли – это две ветви ее эволюции. На нижней ветви гистерезисной петли, с меньшим значением производства энтропии, эволюция системы протекает по термодинамическому принципу Клаузиуса путем образования все более сложных структур с нарастающими значениями их энтропии, что не противоречит теории эволюции Дарвина.

A thermodynamic system (in brief, a system) is any macroscopic material object of thermodynamic research isolated from the (external) surroundings by a control surface. A thermodynamic system whose control surface prevents the mass and energy exchange with the environment is referred to as an isolated system. All other systems that do not meet the isolation conditions will be referred to as open systems.

The thermodynamic processes in the system are a combination of its continuously changing states. If at least one of the process parameters changes, then the state of the system also changes. The processes occurring in a thermodynamic system can be divided into equilibrium and non-equilibrium. Equilibrium processes are those that can be represented as a continuous sequence of equilibrium states in which all parts of the system at any time have the same temperature, pressure, density, concentration, and other parameters. Non-equilibrium processes are those in which the thermodynamic system is not in equilibrium, and therefore the values of the parameters in different parts of the system are different.

Any non-equilibrium process is irreversible, and any equilibrium process is reversible [1]. Reversible processes are those, which, either in the direct or reverse form, cause a thermodynamic system to return to its original state without any changes in the environment. Irreversible processes are those, which, either in the direct or reverse form, do not make a system return to its original state. The reason for the irreversibility of real-life processes lies in their disequilibrium. Reversible processes do not exist in nature.

In 1865, Rudolf Clausius introduced a physical value  $S$ , which he called entropy, into thermodynamics. Its value depends on the state of the system, and it changes only under the influence of energy transmitted in the form of heat. The analytical expression connecting the change in entropy  $dS$  in the equilibrium process with the amount of heat  $\delta Q$  transferred in the process has the form  $dS = \delta Q / T$ . According to the second law of thermodynamics, the change in entropy  $dS$  is equal to or greater than the value of the elementary normalized heat  $\delta Q / T$  absorbed by the system:

$$dS \geq \delta Q / T. \quad (1)$$

The equal sign in (1) refers to equilibrium processes, and the greater-than sign refers to non-equilibrium processes. For isolated systems that by definition do not exchange heat with the environment ( $\delta Q = 0$ ), equation (1) takes the form

$$dS \geq 0. \quad (2)$$

So, no matter what processes occur in an isolated system, its entropy cannot decrease. The equal sign in formula (2) corresponds only to reversible (equilibrium) processes. It follows that in an isolated system spontaneous processes can continue until the entropy of the system reaches the maximum. Upon reaching the equilibrium state, which corresponds to the maximum possible value of entropy for a given system, spontaneous processes in the system subside.

For open thermodynamic systems, the change in entropy  $dS$  consists of two parts

$$dS = d_e S + d_i S. \quad (3)$$

The first part,  $d_e S$ , is the change in entropy due to the interaction of the system with the environment. The second part  $d_i S$  is determined by the processes inside the thermodynamic system itself. The increment of entropy  $d_i S$  cannot have a negative value. The value of  $d_i S$  equals zero only when there are reversible changes in the system, but it is always positive if the processes are irreversible. Thus:

$$d_i S = 0 \text{ (reversible processes),} \quad (4)$$

$$d_i S > 0 \text{ (irreversible processes).} \quad (5)$$

Taking into account that for an isolated system, the entropy flux  $d_e S = 0$ , based on (3) – (5) we write

$$dS = d_i S \geq 0 \text{ (isolated system).} \quad (6)$$

It follows that in such a system, entropy cannot decrease. For isolated systems equation (6) is equivalent to equation (2).

The parameters of a non-equilibrium thermodynamic system change over time at points in space limited by the control surface of the system. The resulting gradients of these parameters, for example, pressure, temperature, concentration, velocity cause the transfer of mass, momentum, energy, etc., which increases the amount of entropy created (produced) inside the system, evens out its heterogeneities and brings the system closer to equilibrium. Thus, a non-equilibrium system is characterized not only by different values of spatial thermodynamic parameters, including entropy, but also by the rate of their temporal changes. Therefore, when describing a system, time becomes a variable. Let us differentiate expression (3) with respect to time  $t$ :

$$dS / dt = d_e S / dt + d_i S / dt , \quad (7)$$

where  $dS / dt$  is the rate of total entropy change;  $d_e S / dt$  is the rate of system-environment entropy transfer;  $d_i S / dt$  is the rate of entropy production inside the system. The component  $d_e S / dt$  accounts for the environment-system transfer processes and can be both positive and negative. The component  $d_i S / dt$  cannot be negative:

$$d_i S / dt \geq 0 . \quad (8)$$

Equality in (8) is applicable to equilibrium processes. In non-equilibrium processes, the rate of production (increment) of entropy can only be positive. The justified confirmation of (8) can be found, for example, in [2, 3]. Further on in the paper, we will refer to the entropy production as

$$P \equiv d_i S / dt . \quad (9)$$

Entropy production is equal to the amount of entropy produced (occurring) inside a thermodynamic system per unit time.

In an isolated system, there is no entropy exchange between the system and the environment, which means that the component  $d_e S / dt$  is absent in (7). Based on this and (8) for an isolated system, we write

$$dS / dt = d_i S / dt \geq 0 . \quad (10)$$

An isolated system can only do work when it is in a non-equilibrium state. As work progresses, the non-equilibrium isolated system will approach the equilibrium state in which the entropy of the system reaches its maximum value, and the entropy production becomes equal to zero. Clausius considered the Universe to be

an isolated system and believed that the entropy of the Universe tends to the maximum, which will ultimately lead to its "thermal death".

So the evolution of an isolated non-equilibrium thermodynamic system is determined by the processes that conform to the following conditions

$$S \rightarrow S_{\max}; d_i S / dt > 0 . \quad (11)$$

Upon reaching the equilibrium state consistent with the extreme conditions:

$$S = S_{\max}; d_i S / dt = 0 , \quad (12)$$

the evolution is complete.

Evolution in thermodynamics is regarded as the process of directional change in the state of a thermodynamic system. Criteria for evolution are the identified relationships, patterns, schemes, algorithms, and other conditions that determine the direction or route of development for a given system.

For any process to begin in a system in equilibrium, this system must interact with its environment. In this case, the transition of the newly formed open thermodynamic system to a new equilibrium state will depend on the conditions of its interaction with the environment. Depending on these conditions, the process of evolution of the system to an equilibrium state may correspond to the extreme value of a thermodynamic function. The examples of such functions are internal energy, enthalpy, Gibbs or Helmholtz free energy. All these functions, which reach extreme values at the equilibrium with the environment, are called characteristic functions or thermodynamic potentials. For example, if, when interacting with the environment, the volume  $V$  and temperature  $T$  of the system are constant, during evolution the Helmholtz free energy  $F$  tends to a minimum, reaching it in equilibrium. Thus, during the evolution of an open system where  $V = const$  and  $T = const$ , the condition  $dF \leq 0$  is fulfilled, while in equilibrium

$$F = F_{\min}; dF = 0; d^2F > 0.$$

It is evident that these conditions differ from the equilibrium conditions (12) for an isolated system. The conditions for the interaction of the system with the environment, under which other characteristic functions in the equilibrium state reach extreme values, are given, for example, in [1, 3].

It should be noted that processes can be considered equilibrium if they occur with infinitesimal deviations from the equilibrium state. Equilibrium processes are the idealization of real processes. However, only the equilibrium states of thermodynamic systems and the processes of their change can be quantitatively described using the methods of classical thermodynamics. In nature, the evolution of any non-equilibrium state to an equilibrium state is caused by irreversible processes. In equilibrium state, these processes cease.

In open thermodynamic systems with irreversible processes and stationary non-equilibrium states, there exist extreme conditions and evolutionary criteria. A stationary state of a non-equilibrium thermodynamic system is a state where all the parameters of the system in its various parts remain unchanged over time, including the total entropy of system  $S$ . We will write equations (3) and (7) for the stationary state in the system

$$dS = d_e S + d_i S = 0; dS / dt = d_e S / dt + d_i S / dt = 0 . \quad (13)$$

For an open continuous system (Fig. 1) in the stationary state, let us write the following using (13)

$$d_i S / dt + d_e S / dt = d_i S / dt + (J_{S,in} - J_{S,out}) = 0 , \quad (14)$$

where  $J_{S,in}$  and  $J_{S,out}$  are total entropy fluxes: inward and outward flows. Entropy flux is the amount of entropy passing through the control surface per unit time. Based on (14), several important conclusions can be made. Since  $d_i S / dt > 0$ , entropy exchange with the surroundings is  $d_e S / dt < 0$ . Thus, the stationary non-equilibrium state in the open system is sustained by the negative entropy (negentropy) exchange with the surroundings. At the same time  $|d_e S / dt| = =d_i S / dt$ .

Entropy production in a stationary non-equilibrium system can be determined using the balance of inward and outward entropy fluxes

$$P \equiv d_i S / dt = J_{S,out} - J_{S,in} . \quad (15)$$

It follows from (15) that stationary non-equilibrium states cannot appear in isolated systems, as stationary state requires entropy flux. Stationary state should not be confused with equilibrium state, where entropy rate is zero.



Fig. 1. Open continuous system

The evolution of non-equilibrium thermodynamic systems and the irreversible processes in them are considered in non-equilibrium thermodynamics or, in other words, the thermodynamics of irreversible processes. Since almost all processes in nature and technology are irreversible, non-equilibrium thermodynamics requires in-depth study.

At present, only non-equilibrium systems in a state close to equilibrium are well researched, since in this case the relations between the thermodynamic flows  $J_\alpha$  in these systems (for example, such as heat fluxes, substances, rates of chemical reactions, etc.) and the flow-inducing forces  $X_\alpha$  (temperature, concentration, chemical affinity gradients, etc.) can be represented as linear equations:

$$J_\alpha = \sum_{\beta} L_{\alpha,\beta} X_\beta , \text{ где } \alpha, \beta = 1, 2 \dots n \text{ for } n \text{ flows и } n\text{-forces.} \quad (16)$$

The coefficients  $L_{\alpha,\beta}$  are called phenomenological, and for  $\alpha = \beta$  they are called eigenvalues corresponding, for example, to the coefficients of thermal conductivity, diffusion, chemical resistance, etc. Due to the linear character of equations (16), this section of thermodynamics began to be called linear non-equilibrium thermodynamics. Its theoretical basis is the Onsager reciprocal relations and Prigogine's theorem on the minimum entropy production, and the main postulate is the presence of local thermodynamic equilibrium at each point in the system.

The physical meaning of the Onsager reciprocal relation is that the influence of the force  $X_\beta$  on the flow  $J_\alpha$  in equations (16) is the same as the effect of the

force  $X_\alpha$  on the flow  $J_\beta$ . This corresponds to the equality of the coefficients  $L_{\alpha,\beta} = L_{\beta,\alpha}$  in (16). When only two thermodynamic forces are active, the influence of the first force (e.g. temperature gradient) on the flow (e.g. diffusion) caused by the second thermodynamic force is the same as the influence of the second thermodynamic force (concentration gradient) on the flow of the first force (heat flux). Onsager's theory makes it possible to explain the internal relationships between various effects and predict new processes. When the values of the coefficients  $L_{\alpha,\beta}$  are determined experimentally, the theory allows establishing a quantitative relationship between simultaneous processes in the system, even without detailed information about their mechanism.

Let us consider several well-known processes explained by Onsager's theory: thermoelectric effect – when the junction of two dissimilar metal conductors is heated, a potential difference appears across their ends; thermal diffusion – a concentration gradient of components appears under the influence of a temperature gradient; barodiffusion – diffusion flows appear under the influence of a pressure gradient. A list of known cross-over phenomena is given in [4]. An analytical substantiation of some of the effects can be found in [3].

A derivation of Prigogine's theorem with assumptions is given in [2]. In [5], a brief description of the results following from Prigogine's theorem is given: "If stationary states occur close enough to equilibrium, they can be characterized by the extremal principle, according to which the production of entropy reaches a minimum value in a stationary state compatible with the given conditions (constraints), which are determined by the nature of the problem". "The theorem on the minimum entropy production is valid only in the field of linear thermodynamics of irreversible processes, also provided that the phenomenological coefficients can be considered constants that fulfil Onsager reciprocal relations".

Let us give an alternative formulation of Prigogine's theorem.

In an open macroscopic thermodynamic system in a stationary state close to thermodynamic equilibrium, under constant external conditions, the value of entropy production due to internal irreversible processes in the system has a minimum positive value provided that the Onsager reciprocal relations are fulfilled in linear equations describing these processes.

Therefore, according to the theorem, the state of a linear open system with time-independent boundary conditions changes toward decreasing entropy production until, in the end, a stationary state with a minimum entropy production value is reached. Consequently, the process of evolution of a non-equilibrium thermodynamic system under consideration fulfils the conditions

$$S \rightarrow S_{St} < S_{\max}; P \equiv d_i S / dt \rightarrow P_{\min},$$

where  $S_{St}$  is entropy in the stationary non-equilibrium state;  $S_{\max}$  is maximum entropy if the system transits into equilibrium;  $P_{\min}$  is minimum entropy production in the stationary state.

When the stationary non-equilibrium state is reached conforming to the extreme conditions:

$$d_i S / dt = P_{\min} > 0; dP / dt < 0 ,$$

the system evolution is complete. The above conditions indicate the stability of the stationary state with the minimum entropy production [3]. This means that if fluctuations increase the value of  $P$ , the internal non-equilibrium processes restore  $P$  to its minimum stationary value. Prigogine's theorem is confirmed by examples for various physical and chemical non-equilibrium processes (for example [3, 6]).

Nature has plenty of systems that are far from equilibrium and to which the relations of linear non-equilibrium thermodynamics are not applicable. The evolution process of such systems is mainly studied using a method based on a direct description of the processes according to the laws of nature. In this case, the postulate of local equilibrium is used, which can serve as the basis for representing thermodynamic variables as functions of the spatial and temporal position. With this postulate, differential equations can be used to describe the processes in non-equilibrium thermodynamic systems. For the vast majority of non-equilibrium systems, differential equations are nonlinear and contain coefficients that can be determined only experimentally. In this case, the possibility and ways of achieving a particular stationary state are determined by the initial and boundary conditions, as well as the type of differential equations, if they correctly reflect the laws existing in the system. In this case, the state of the system is not always unambiguously determined by the equations and the investigation of their stability.

It should be noted that thermodynamic systems far from equilibrium could have several stationary states that differ not only in the thermodynamic parameters of the system, but also in their structures. Transitions from one non-equilibrium stationary state to another are realized through non-stationary states characterized by fluctuations in parameters and temporal and spatial changes in the structure of the system. In addition, such non-equilibrium systems can develop "unpredictably", in particular, acquire different stationary states under the same boundary conditions, which makes it difficult to describe them using differential equations. For these systems far from equilibrium, the extremal principles described above, predicting the states to which the systems pass, are not applicable as well. In the absence of the extremum principle, it becomes impossible to unambiguously determine which stationary state a particular non-equilibrium system will assume. It should also be noted that the application of the postulate of local equilibrium to a non-equilibrium process is incorrect, since it is assumed that the state of a small volume is described by equations not dependent on thermodynamic forces (gradients) and flows.

Based on the above, when considering evolution in various physical, chemical and biological non-equilibrium thermodynamic systems, the author used experimental data, integral conservation equations to describe the processes, known thermodynamic positions and calculation methods, including entropy. For example, integral conservation equations were employed to describe the evolution of stationary non-equilibrium thermodynamic systems in which hydro-gas-dynamic and aerodynamic processes take place. In this case, the boundary of the system was selected in such a way that the distribution of the thermodynamic parameters of the inward and outward flows at the boundary were known or calculated using integral

equations. This made it possible to determine the entropy flux entering the system  $J_{S,in}$ , and the entropy flux exiting the system  $J_{S,out}$ , and the production of entropy  $P$  in a stationary non-equilibrium system using (15).

In [7-15] it is shown that non-equilibrium processes in fluid dynamics, heat exchange, aerodynamics, magnetism, heterogeneous catalytic and homogeneous periodic chemical reactions, in biological systems (in the cell membrane, protein and algae cell), as well as in the Earth's atmosphere, conform to the same general laws of changes in the states of non-equilibrium thermodynamic systems in the process of their evolution. These regularities are based on the general principle formulated in [14] in the form of an axiom about the processes in nature striving for perfection: *of all possible stationary states of the system allowed by natural forces, thermodynamics of irreversible processes, boundary and other physically justified conditions, the most probable is the state with the lowest possible entropy production.*

This axiom was formulated based on experimental studies of mixing processes of single-phase and two-phase flows in fluid dynamic systems [15] and has now been confirmed for a number of other processes occurring both in physical, chemical and biological systems.

In the axiom, the possible stationary states of a thermodynamic system mean all stationary (quasi-stationary) states that can be realized in the course of its evolution. The states of the system allowed by the thermodynamics of irreversible processes are those stationary states for which the total production of entropy, and for some systems, also its constituent parts (caused, for example, by the equalization of the velocities of the mixing flows and the friction of the flow against the wall) have positive values [15]. With this in mind, for some systems, the minimum permissible entropy production corresponding to a stationary state can also be determined. Parameters at the boundary of the selected thermodynamic system are assumed as boundary conditions. Other physically substantiated conditions are regarded as those conditions, which allow stationary states with the minimum possible production of entropy to appear and exist. For different thermodynamic systems, these conditions are different, but they have several features in common.

Prigogine's theorem can be viewed as a special case of the axiom proposed. This theorem is applicable to a thermodynamic system with only one stationary state, close to equilibrium, when the Onsager relations are observed. Only in this case, the extremal principle of minimum entropy production proposed by Prigogine can be applied to determine the stationary state of the system.

The axiom is applicable to any non-equilibrium thermodynamic systems with one or several stationary states that differ in the values of entropy production. In this case, the axiom does not use the principle of extremality to determine the realizable stationary state, in contrast to Prigogine's theorem. It should be noted that there does not exist a thermodynamic potential, whose extremality determine the behavior of the system far from equilibrium. In thermodynamic systems with several stationary non-equilibrium states, each of them corresponds to its own, quite

definite value of entropy production. Moreover, the farther the stationary state is from the equilibrium state, the greater the value of the entropy production corresponding to it. According to the axiom, under certain conditions, out of all possible stationary states of the system, the realization of a state with the minimum possible production of entropy is most probable.

Let us consider some problems solved using the axiom. In [7] (problem 2), it is shown that when seawave captures a fixed mass of air with a volume of indefinite shape, and the shape of this volume surrounded on all sides by water is subsequently transformed, the stationary state with the minimum possible value of entropy production is a spherical shape. It is the bubble shape that a stationary air volume in water assumes in nature.

It is shown in [9] that in an isolated thermodynamic system comprised of iron and the environment, the production of entropy for magnetized iron is less than for non-magnetized iron. Therefore, according to the axiom, the probability of iron being in nature in a magnetized state is higher than in a non-magnetized state. The presence of large masses of magnetic iron ore under the surface of the Earth is the cause of magnetic anomalies (for example, the Kursk Magnetic Anomaly).

Let us present the experimentally and theoretically proven general regularities of changes in the states of a thermodynamic system with at least two non-equilibrium stationary states, which confirm the validity of the axiom.

*1. The transition of a non-equilibrium thermodynamic system from a lower to a higher entropy production state occurs only if a physically substantiated condition is violated in the course of its evolution, if this condition is not fulfilled, the initial state cannot exist. In this case, from all possible states with a high production of entropy, the transition proceeds to the state with the minimum possible production of entropy, provided such a transition is allowed by physical conditions.*

*2. The transition of a non-equilibrium thermodynamic system from a higher to a lower entropy production stationary state occurs when, during the evolution of the system, the difference in the entropy production of these two states reaches a certain positive value.*

*3. Direct and reverse transitions between two stationary states of a non-equilibrium thermodynamic system are characterized by hysteresis. During these transitions, the structures corresponding to the states and the thermodynamic parameters change abruptly, intermittently.*

*4. The process of transition of a non-equilibrium thermodynamic system between stationary states occurs through non-stationary states, which can smooth out the abruptness of the transition.*

*5. The lower the production of entropy in the stationary state of a non-equilibrium thermodynamic system, the more there are physical conditions essential for its implementation.*

Using some non-equilibrium thermodynamic systems as an example, we will demonstrate the general laws of their evolution. Let us start by considering hydrodynamic processes in non-equilibrium systems. In [7], a cylindrical pipe of a

certain length with a gas flowing at a specified rate is considered as a thermodynamic system. The laws of nature allow two stationary states of such a system, corresponding to laminar and turbulent flow regimes. Each of the modes has its own profile of the flow velocity over the pipe section and law of friction of the flow against the wall. Fig. 2 shows calculated specific entropy production for laminar  $IIS_L$  and turbulent  $IIS_T$  flow regimes as functions of the Reynolds number  $Re$ . The specific production of entropy  $IIS$  is the amount of entropy that occurs within the system per unit time, taken relative to a unit flow rate. When constructing these dependencies, the integral equations of conservation of mass, momentum and energy for the considered section of the pipe were solved, presented in a form that takes into account the non-uniform distribution of parameters (in this case, velocity) over the section [7, 15].

Fig. 2 demonstrates that the production of entropy for a laminar flow is less than for a turbulent flow. In accordance with the axiom, of the two possible stationary states of a thermodynamic system, the most probable is the state with the minimum possible entropy production, which in this case corresponds to the laminar regime realized at small values of  $Re$ . According to the general laws, a thermodynamic system can pass from a state with the minimum possible entropy production to a state with a higher entropy production only if a physically justified condition is not fulfilled. Such a physical condition for this system is the resistance of the laminar flow to internal or external disturbances. In the absence of disturbances, the laminar flow structure formed at the beginning of the flow must exist, according to the axiom, for any values of  $Re$ . However, the higher the value of  $Re$ , the weaker disturbances lead to the loss of stability of the laminar motion, and once they arise, they no longer subside but intensify with time. In Fig. 2, the arrow marks the transition from laminar to turbulent flow at the upper critical value of the Reynolds number  $Re_{CR} \approx 9000$ . It is indicated in [16] that the upper critical value of  $Re$  has not been finally determined. In some experiments, it reached the value  $Re_{CR} = 5 \cdot 10^4$ .

According to the general laws given above, the transition of a non-equilibrium thermodynamic system from a lower to a higher entropy production state should be accompanied by rather sharp, abrupt changes in both the flow structure and other parameters. This is confirmed by experiments, according to which the transition of a laminar flow regime to a stable turbulent regime occurs through unsteady states in a certain narrow range of the Reynolds number close to the critical value. In this case, in the system under consideration, a continuous, chaotic change is observed both in time and in the flow regions with a turbulized and laminar moving gas. This phenomenon is known as "intermittency" [16].

According to the axiom, of the two states of a thermodynamic system, the state with a minimum entropy production is most probable, but for it to be realized, certain physical conditions must be fulfilled. In the case under consideration, with a decrease in the  $Re$  number, the transition of a thermodynamic system from a state with a higher entropy production (turbulent flow) to a state with a lower production (laminar flow) occurs when a certain positive difference between the entropy

production of these states in their evolution is reached. In experiments, such a difference in the production of entropy for the problem under consideration is achieved at the lower critical value  $Re'_{CR} = 1700 - 2500$  (Fig. 2). There exists prominent hysteresis between the direct transition from the laminar regime to the turbulent regime ( $Re_{CR} \approx 9000$ ) and the reverse transition from the turbulent to the laminar regime. At Reynolds numbers less than the lower value  $Re'_{CR}$ , the motion in the pipe remains laminar at any disturbances introduced into the flow.

From the above, it follows that the behavior of the considered thermodynamic system fully corresponds to the general laws of the evolution of non-equilibrium thermodynamic systems. The axiom formulated above makes it possible to explain the laminar to turbulent transition and the reverse one from the standpoint of non-equilibrium thermodynamics. It can also answer the question why the laminar to turbulent transition can occur at a critical Reynolds number much greater than the reverse turbulent to laminar transition.

Another example of a non-equilibrium thermodynamic system is a mass of water in a large volume at atmospheric pressure boiling under natural convection on a flat heat-emitting bottom of a vessel bounded by thermally insulated sidewalls [8]. Experiments have established several possible boiling regimes in such a system. There are two main regimes: nucleate boiling and film boiling. The transition from one boiling regime to another is determined by the density of the heat flux  $q$ , which represents the amount of heat passing through a unit area of the heat-transfer surface per unit of time. Based on the experimental data presented in [17, 18], the specific production of entropy  $IIS$  for the nucleate and film boiling regimes were determined as functions of  $q$ . These dependences are shown in Fig. 3. In the case under consideration, the specific production of entropy is the amount of entropy produced per unit time per unit area of the heat-transfer surface. The developed nucleate boiling regime corresponds to a lower value of the specific entropy production, and the film boiling corresponds to a higher value. These boiling modes are distinguished by the vaporization pattern – the hydrodynamic structure near the heat-transfer surface. With developed nucleate boiling, a large number of vaporization centers are formed on the heat-transfer surface. However, in this case, the liquid continues to flow around the heating surface among these centers, and its boundary layer is intensively mixed by the vapor bubbles in it. During film boiling, the liquid is separated from the heat-transferring surface by the resulting layer of water vapor with a lower thermal conductivity, subsequently, the intensity of heat transfer becomes many times lower than during nucleate boiling.

The transition from the nucleate regime to the film boiling regime occurs when the heat flux density reaches the first critical value  $q_{CI}$  (Fig. 3). This transition from a state with a lower specific production of entropy to a state with a higher production is discontinuous, accompanied by an abrupt change in both the hydrodynamic pattern near the heat-transfer surface and thermodynamic and thermophysical parameters. It is similar to the transition from a laminar to a turbulent flow regime (Fig. 2), accompanied by an abrupt change in the

hydrodynamic pattern of the flow and the resistance to the flow. The considered transition from a stationary state with a lower entropy production to a higher production state, as for other non-equilibrium systems, is characterized by a nonstationary boiling pattern. All sorts of combinations of film and nucleate boiling regimes are formed in different, randomly changing places of the heat-transfer surface. This resembles the regime of a laminar to turbulent transition in a pipe, where chaotic temporal and spatial changes are also observed in the flow regions with turbulent and laminar moving gas. The transition from nucleate boiling to film boiling is associated with the loss of the hydrodynamic stability of the two-phase near-wall layer due to the growth of vaporization centers with increasing  $q$  [17]. This is analogous to a laminar flow losing resistance to internal or external disturbances in the flow. It was also shown in [17] that by slowly increasing the heat flux through a specially selected heat-transfer surface depleted of vaporization centers, it was possible to exceed in some experiments the normal critical value of  $q_{CI}$  by almost two times. This resembles an increase in the value of the upper critical Reynolds number ( $Re_{CR}$ ), at which the laminar flow becomes turbulent, by reducing the disturbances introduced into the flow.

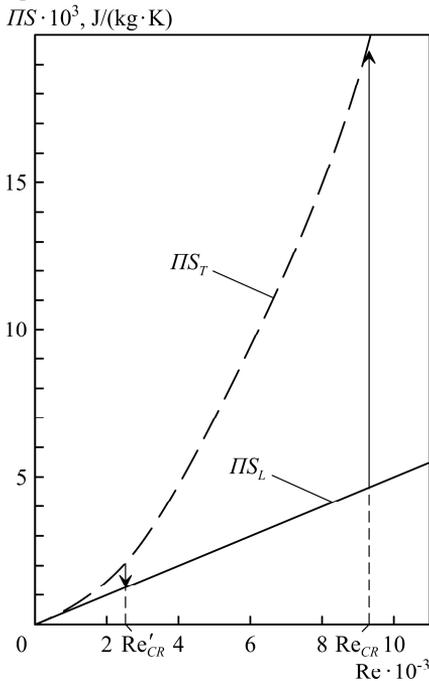


Fig. 2.  $IIS$  as a function of  $Re$  number for laminar  $IIS_L$  and turbulent  $IIS_T$  (flow rate profile 1/7) flow regimes

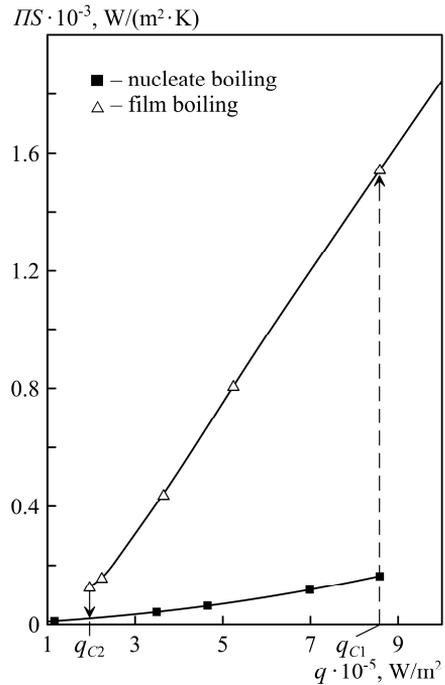


Fig. 3.  $IIS$  as a function of  $q$  for two boiling regimes in a large volume of water ( $P = 0.1$  MPa)

The curves in Fig. 3 demonstrate that the reverse transition of a thermodynamic system from a higher to a lower entropy production state occurs when the difference between the entropy production in these two states reaches a certain positive value. This corresponds to a decrease in the heat flux density up to

the second critical value  $q_{C2}$ , which is much lower than  $q_{C1}$ . Thus, hysteresis is clearly pronounced in the thermal and hydrodynamic phenomena associated with the transition from one boiling regime to another. From the above, it follows that the non-equilibrium system with heat exchange processes conforms with the same general laws of evolution from the standpoint of non-equilibrium thermodynamics.

Let us analyze the applicability of these general laws to the Rayleigh-Benard convection process considered in detail in [7]. Convection occurs in a horizontal liquid layer with a vertical temperature gradient created by heating the layer from below. Depending on the heating temperature, or rather, the Rayleigh number  $Ra$ , the following forms of various stationary (stable) states of fluid movement appear in the layer: Benard cells; two-dimensional cells resembling the rotation of shafts in opposite directions; three-dimensional cells and other organized structures. Each stationary state has its own value of entropy production, and transitions from lower to higher entropy production states occur when certain critical values  $Ra_1$ ,  $Ra_2$ ,  $Ra_3$ , etc. are reached. Fig. 4 shows the nature of the change of entropy production as a function of  $Ra$  for four stationary states. With weak heating of the fixed layer from below, when the temperature difference across the layer is small, the supplied heat is completely removed by means of thermal conductivity, and there convective flows are absent. This state corresponds to Curve 0 in Fig. 4. With the heating temperature increasing, convective flows appear and when the value of  $Ra_1$  is reached, a new stationary state of a non-equilibrium system is formed with a honeycomb-like structure of fluid movement (Benard cells). This case corresponds to Curve 1 in Fig. 4. With a further increase in the heat flux, the formed flow structure is first preserved, and then the Benard cells begin to collapse with non-stationary states forming. At the Rayleigh number  $Ra_2$  the thermodynamic system passes to a new stationary state, for example, with a roll structure of fluid flow. This flow corresponds to Curve 2 in Fig. 4. At the Rayleigh number  $Ra_3$ , a new stationary flow structure is formed, and so on.

Fig. 4 demonstrates that with an increase in the value of the Rayleigh number, the thermodynamic system transits from a state with a lower entropy production to a state with a higher entropy production. In this case, the transition, according to the above axiom, is carried out due to the failure of some physically justified condition. So the transition from the stationary state to the Benard convection state occurs at the number  $Ra_1$  caused by the thermocapillary instability of the liquid layer. Experiments [19] showed that with a decrease in the inward heat flux, and hence a decrease in the Rayleigh number, the thermodynamic system under consideration will undergo a reverse transition from a higher to a lower entropy production stationary state at lower Rayleigh numbers than for direct transition. In Fig. 4, the reverse transitions correspond to the Rayleigh numbers marked with a prime symbol:  $Ra'_1$ ,  $Ra'_2$ ,  $Ra'_3$ . Thus, transitions between two stationary states of a non-equilibrium thermodynamic system exhibit hysteresis, as in other systems we considered. In this case, the transition of a thermodynamic system from a higher to a lower entropy production state occurs when a certain positive difference between the production of entropy in these states is reached. It follows that the above axiom

and the conclusions drawn from it fully apply to the system under consideration. Even during the transition from a state with a lower entropy production to a higher production state, if several such stationary states exist, the thermodynamic system will first pass to the state with the lowest possible entropy production value of all, if physically justified conditions allow this. If the conditions do not allow this, then the system will pass into the next state, which has the minimum production of entropy of all remaining states. For example, if the flow of a liquid corresponding to Benard convection cannot be formed because at least one of the many conditions for the implementation of such a flow cannot be fulfilled, then when the liquid is heated, the stationary state will transform into a roll flow, which is a more common form of stationary convection.

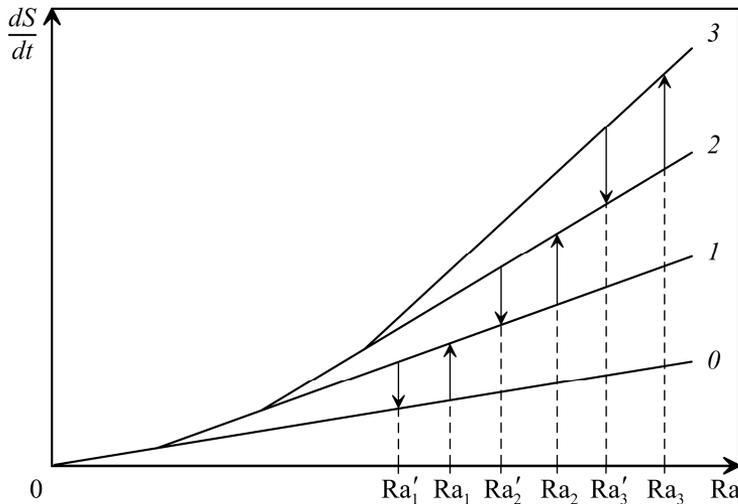


Fig. 4. Change in entropy production as a function of the Rayleigh number

When considering the process of the origination of Benard convection, the authors of [20] noted that when such a stationary state is established, "the production of entropy in the system increases, which contradicts Prigogine's theorem of minimum entropy production". However, as follows from the above, this does not contradict the proposed axiom of processes in nature striving for perfection.

The work [10] analyzes the processes occurring when air flows around a cylinder and an aircraft wing. It is shown that thermodynamic systems where aerodynamic processes take place conform to the same general laws of evolution of macroscopic non-equilibrium systems as above. Also transitions from a stationary state with a lower entropy production to a state with a higher production and back are realized through hysteresis. The transition process occurs quite abruptly, intermittently, through the formation of non-stationary states.

For example, when the air flows around a small wing, two stationary states of the thermodynamic system are realized, each of them has its own flow pattern near its surface, its own drag and lift coefficients of the wing, and, accordingly, its own values of entropy production. Fig. 5 shows specific entropy production as a function

of the incoming airflow speed, or rather the Reynold number, calculated from the chord airfoil length. The greater value of the entropy production  $IIS_2$  corresponds to the flow pattern around the wing with the separation of the boundary layer from its upper surface. The separation of the boundary layer leads to an increase in drag and a decrease in lift. The lower value of the entropy production  $IIS_1$  (Fig. 5) corresponds to the nonseparated flow around the upper surface of the wing. This leads to a decrease in drag and an increase in lift in comparison with a separated flow. Therefore, by organizing the turbulization of the boundary layer at the tip of the wing in various ways, it is possible to delay the transition of the thermodynamic system from the state with to a lower entropy production to a state with a higher production. This has been confirmed by numerous experiments, for example, with the use of a tripping wire at the beginning of the wing or appropriate changes in the shape of the wing tip.

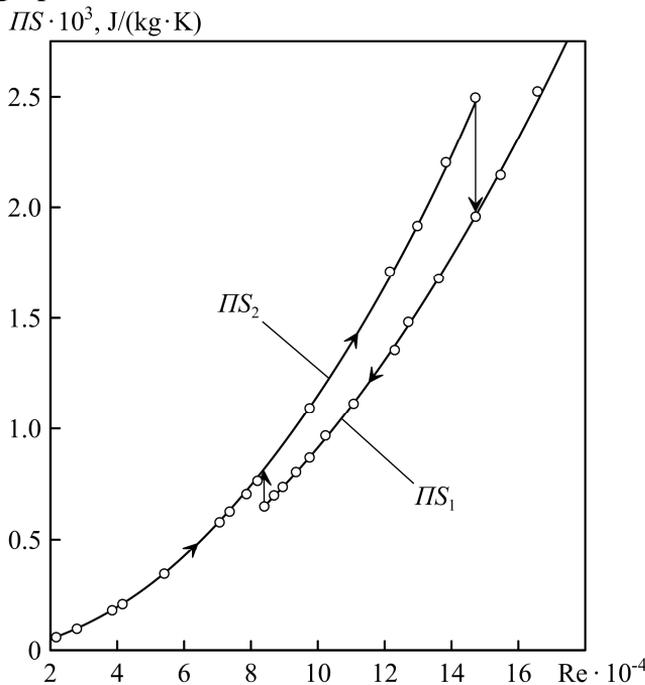


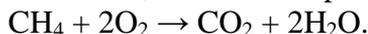
Fig. 5.  $IIS$  as a function of  $Re$  number for the wing flow pattern

Life forms also strive for perfection when creating certain conditions. For example, in order to fly with a turbulized boundary layer corresponding to a state with lower entropy production, a bird's wing has a suitable profile and greater relative roughness, just like the wings of some insects. The wing of a dragonfly has transverse folds for turbulization of the boundary layer, and its leading edge is equipped with sharp teeth. All this confirms the validity of the axiom about the processes in nature striving for perfection.

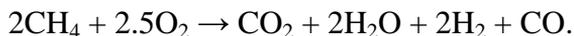
It was shown in [10] that both "left" and "right" hysteresis can be realized in aerodynamics depending on the variable parameter (argument) in the experiment and the corresponding selected function. With a "left" hysteresis, with an increase

in the argument and its subsequent decrease, the function values change counterclockwise, and with a "right" hysteresis – clockwise.

In [11] the results of experimental studies of concentration hysteresis in the reaction of low-temperature methane oxidation on a dispersed Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst are analyzed from the standpoint of non-equilibrium thermodynamics. Fig. 6 shows the specific production of entropy  $IIS_1$  and  $IIS_2$  as functions of different O<sub>2</sub> concentrations in the initial reaction mixture (IRM), respectively, for the lower and upper branches of the hysteresis loop. On the lower branch of the loop, with the catalyst in an inactive state, only the products of complete oxidation of methane CO<sub>2</sub> and H<sub>2</sub>O are formed, which corresponds to the reaction



In this case, the degree of conversion of methane CH<sub>4</sub> remains practically constant and equals 28%. On the upper branch of the hysteresis loop, with the transition of the catalyst to the active state, along with the products of complete oxidation, the products of partial oxidation of methane H<sub>2</sub> and CO also appear, which corresponds to the reaction



In this case, the degree of methane conversion can reach 99%, depending on the O<sub>2</sub> concentration in IRM. The transitions from the lower branch of the hysteresis loop to the upper branch and in reverse occur abruptly, practically intermittently. In the process of transition of a thermodynamic system from one stationary state to another, non-stationary structures are formed, which can be various combinations of stationary structures of the beginning and end of the process, chaotically changing in time and space.

It is also shown that the justified condition allowing a state with a minimum entropy production  $IIS_1$  is a certain ratio of the O<sub>2</sub>:CH<sub>4</sub> concentration in the IRM, which enables the corresponding reaction in the thermodynamic system under consideration. Experiments also showed that with a decrease in the oxidation temperature of methane, the ratio of O<sub>2</sub>:CH<sub>4</sub> concentrations in IRM that allows complete methane oxidation decreases, and the thermodynamic system transits into a state with a higher entropy production  $IIS_2$ . During this transition, the catalyst is activated.

The processes in such biological systems as the cell membrane, single-domain and multi-domain globular proteins, and the cell of the *Chara corallina* alga are analyzed from the standpoint of non-equilibrium thermodynamics in [13]. It is shown that all these processes conform to the general laws of evolution of non-equilibrium thermodynamic systems presented above. For example, Fig. 7 shows the change in the specific production of entropy as a function of the temperature of the membrane from dipalmitoylphosphatidylcholine (DPPC) for gel- ( $IIS_G$ ), intermediate ( $IIS_I$ ), and liquid crystal ( $IIS_{LC}$ ) states. In the thermodynamic system under consideration, three stationary states of the membrane are realized depending on the temperature. These states differ not only in structure, but also in thermodynamic and other parameters and properties. In accordance with Fig. 7, lower to higher entropy production transitions in the system at temperatures  $T_{C1}$  and

$T_{C2}$  and reverse transitions are realized through hysteresis. The transitions are carried out quite abruptly with the formation of non-stationary structures. From the standpoint of non-equilibrium thermodynamics, these transitions are analogous to the transitions described above for Rayleigh-Benard convection.

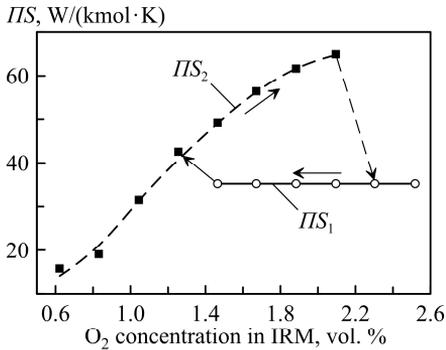


Fig. 6.  $IIS$  as a function of  $O_2$  in IRM ( $CH_4$  concentration in the IRM 1.1 vol. %; reaction temperature 703 K)

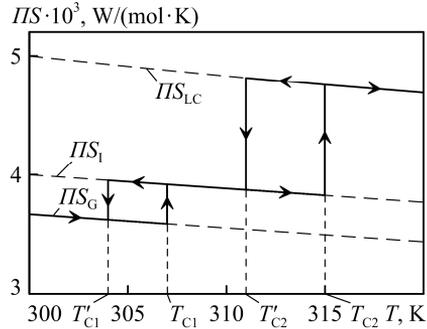


Fig. 7. Change in the specific production of entropy as a function of temperature for gel ( $IIS_G$ ), intermediate ( $IIS_I$ ), and liquid crystal ( $IIS_{LC}$ ) states of the membrane from DPPC

Other thermodynamic systems conforming to the general laws of evolution of non-equilibrium systems, with different physical, chemical and biological processes from above are analyzed in [7-15]. In particular, the processes of interaction of single-phase and multi-phase jets in the mixing chambers of gas ejectors and two-phase jet apparatus are considered; the process of gas flow in a supersonic Laval nozzle; processes during a drag crisis of bluff bodies, in various periodic chemical reactions, including the Belousov-Zhabotinsky reaction; and other processes.

Based on the above, the evolution process of a non-equilibrium thermodynamic system with several possible stationary states is schematically shown in Fig. 8. Here  $IIS_i$  is the specific entropy production corresponding to the  $i$ -th stationary state of the system. In this case,  $IIS_{i+1} > IIS_i$ , where  $i = 1 \dots n$ , and  $n$  is the number of the possible stationary states. Solid and dotted arrows show the transitions from one stationary state to another in the process of increasing or decreasing the independent parameter, respectively. These transitions occur through transient system states and exhibit hysteresis. The independent parameter affecting the evolution of a non-equilibrium system can be, for example, temperature, specific heat flux, concentration of a chemical component, Reynolds or Rayleigh criteria, and many other parameters, depending on the chosen thermodynamic system. The diagram in Fig. 8 is for left hysteresis. For the right hysteresis, it can be constructed in a similar way. It can be seen from the diagram that, for example, with an increase in the independent parameter, transitions are made from one stationary state with a lower entropy production value to another stationary state

with the minimum possible entropy production of all remaining (higher) stationary states with a higher value of entropy production (in accordance with the axiom).

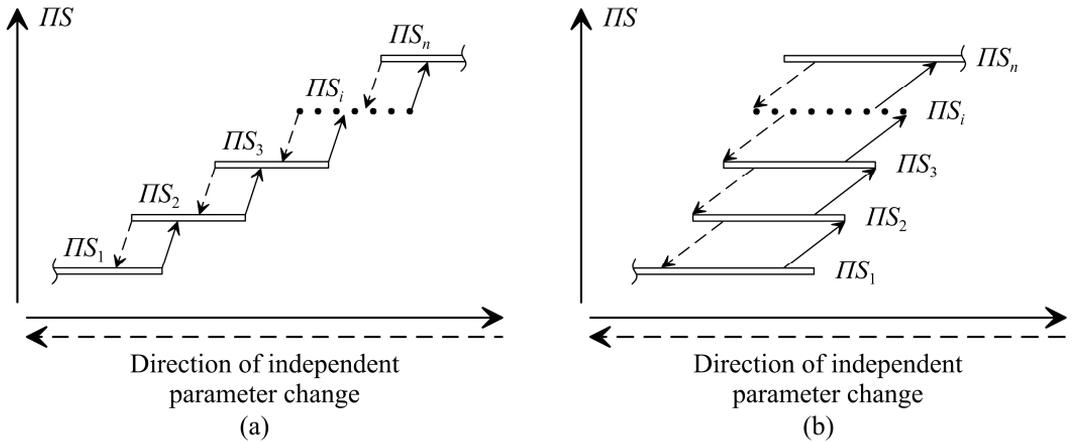


Fig. 8. Schematics of the hysteresis evolution of a system with several stationary states for non-overlapping (a) and overlapping (b) stationary states

Thus, both with an increase and a decrease in the independent parameter, transitions from one non-equilibrium stationary state ( $IIS_i$ ) to another stationary state ( $IIS_{i+1}$  or  $IIS_{i-1}$ , respectively) are carried out with a minimally different value of entropy production from the initial state. Accordingly, the modulus of the difference between the entropy productions of the initial state  $IIS_i$  and the state  $IIS_{i\pm 1}$  into which the system transits should be the minimum of all possible realized stationary states

$$\Delta IIS = |IIS_i - IIS_{i\pm 1}| = \min.$$

Fig. 8a shows a diagram of the evolution of a system with several non-overlapping stationary states. Non-overlapping states are those in which the transitions to the next stationary state occur only after the completion of the transitions to all the previous stationary states. For example, when the temperature of the cell membrane reaches  $T_{C1}$  (Fig. 7), the system transits from a stationary gel state to an intermediate state, and then, with a further increase in temperature to  $T_{C2}$ , the intermediate state transforms into a liquid crystal state. Each of these three stationary states has its own specific structure [13], and until the transition from one state to another is completed, the transition to the next state does not begin.

Overlapping states are such stationary states of the system where transitions to the next state begin before the completion of the transitions to the previous states. Fig. 8b shows a diagram for overlapping stationary states. It corresponds, for example, to the transitions in a multi-domain protein formed, assumably, in the process of Darwinian evolution by alternately combining different single-domain proteins with the same initial values of specific entropy production over time [13].

Nature also knows cyclic methods of evolution [21]. Based on the above, it can be assumed that the cyclic evolution of a thermodynamic system differs from the hysteresis evolution in that on both branches of the evolutionary process, corresponding to both a sequential increase and decrease in the entropy production,

all newly formed stationary states differ in structures and other properties, with the exception of the one with the lowest value of entropy production. It is from this stationary state that the evolutionary cycle begins and ends. This can be traced using the example of the life cycle of the slime mold *Dictyostelium discoideum* [3, 21].

In conclusion, transferring the obtained regularities of the hysteresis process of evolution of non-equilibrium thermodynamic systems to the Earth's atmosphere with all kinds of organisms living in it, we can conclude that glacial and interglacial periods of life on Earth are two branches of its evolution. On the lower branch of the hysteresis loop, with a lower value of entropy production, the evolution of the system proceeds according to the thermodynamic principle of Clausius by the formation of more and more complex structures with increasing values of their entropy and the approach of the system to global chaos. The work [8] shows the influence of some factors, both natural and anthropogenic, that increase the entropy production in the atmosphere and bring the Ice Age on Earth closer.

When the critical value of entropy production is reached, the thermodynamic system abruptly, through non-stationary, chaotically changing structures, moves to the upper branch of the hysteresis loop, and the reverse process of the formation of organized structures from chaos begins with sequentially decreasing values of their entropy production. In this case, the entropy of the entire Earth's atmosphere decreases due to the excess of the heat loss into space, in comparison with its inflow. This can occur, among other things, due to the destruction of the atmospheric layer creating the greenhouse effect by vortex and other circulation flows. When the second (lower) critical value of entropy production is reached, the system abruptly, through non-stationary, chaotic structures, transits to the lower branch of the hysteresis loop and a new stage in the evolution of the system begins, characterized by an increase in the entropy production. Thus, organized, ordered structures are formed out of chaos, and in the process of their development, turn back into chaos.

During the transition from chaos to ordered structures on the lower branch of the hysteresis loop, the development of the animal world proceeds in accordance with the Darwinian theory of evolution. The process of improving all living things occurs through transitions from simpler structures to more complex ones under the influence of natural selection. This indicates the inseparability of the existence of the two principles of Clausius and Darwin in the process of evolution of the considered thermodynamic system.

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